DETERMINATION OF THE OPTIMUM CONDITIONS FOR RECOVERY OF GOLD FROM ZARSHURAN REFRACTORY GOLD SULFIDE ORE

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Abstract: *The orthogonal array design has been used to determine the optimum conditions for gold recovery from Zarshuran refractory gold sulfide ore (Iran) by direct cyanidation and roasting-cyanidation.*
The Taguchi method was used as the experimental design to determine the optimum conditions of dissolution behavior of gold with cyanidation and roasting-cyanidation from Zarshuran refractory gold ore .
The experimental conditions were studied in the range of 10–12 for pH, 20-40 for time(h), 400-1200 for cyanide content (g/ton) and 30 -40 for percent solid(%).
Orthogonal array (OA) L_9 (3^4) consisting of four parameters each with three levels, was chosen. From this study for direct cyanidation the total optimum gold dissolution (30.11%) obtained at pH (10), Time (40 h), Cyanide content (800g/ton) and Percent solid (30%).
Also for roasting- cyanidation the total optimum gold dissolution (34.96%) obtained at pH (12), Time (40 h), Cyanide content (1200g/ton) and Percent solid (35%).

Keywords: *Refractory gold ore; Cyanidation; roasting; Taguchi method .*

1. INTRODUCTION

Now a day, almost all gold produced from ores in the world is extracted by the cyanidation process. This process was recognized as early as 1783 and afterward between 1887 and 1888, [1].

The chemical reaction is called the Elsner Equation as follows[2, 3, 4, 5] :

$$4Au + 8NaCN + O_2 + 2H_2O \rightarrow 4\ Na[\ Au(CN)_2\ ]^- + 4NaOH \quad (1)$$

With depletion of the oxidized free-milling gold reserves, most of the new gold deposits being mined today are sulfide ore which do not recovered easily by direct cyanidation. These types of Gold ores are called refractory if gold extractions from a conventional cyanidation process are less than 80% even after fine grinding [6, 7, 8].

It is found that in refractory sulfide ores gold is very finely disseminated and encapsulated in host matrices that are not in contact with cyanide solution. Also these minerals and specially arsenian sulfide minerals can inhibit gold dissolution by consuming cyanide and oxygen, in competition with gold, or by formation a passive layer on the gold surface.

In the case of such refractory ores, a pre-oxidation step often becomes necessary to oxidise the base metal sulfides and expose the gold particles for subsequent leaching [1, 8, 9].

The main methods of pre-oxidation recommended for the refractory gold ores are roasting, pressure oxidation, chemical leaching and bacterial oxidation [10, 11, 12, 13].

Based on the review literature, all the refractory sulfide ores which have studied up to know are only ores with high content of pyrite, chalcopyrite, arsenopyrite and pyrotite. On the other hand, no information exists about the refractory orpiment ore. So, as Zarshuran mine is almost the only mine with high content of the orpiment, it is decided to study the possibility of direct caynidation and also raosting-cyandiation on recovery of gold from Zarshuran refractory gold ore.

2. EXPERIMENTAL

2. 1. Material and Methods

A sample of about 100 kg Refractory sulphides

Table 1. mineral assemblage of the selected sample.

Mineral	Estimated Volume (%)
Orpiment	76
Silica	20
Calcite	1
Mesquite	1
Gypsum	1
Galena	<0.1
Pyrite	<0.1
Sphalerite	<0.1
Pyrhotite	<0.2

ore was taken from Zarshuran mine in the north west of Iran which considered as a representative sample. After crushing, the sample was ground in a steel laboratory ball mill and semi quantitative analysis is carried out on the sample which the results are indicated in table 1. An X-ray diffraction illustrating the contents of the sample is given in Figure 1. Then, the ore is sieved using ASTM standard sieves, giving particle size fraction less than 70 micron.

Systematic gold particle identification (gold scan) was performed on the polished sections using ore microscopy.

Leaching experiments are conducted in a 1 L spherical glass reactor equipped with a mechanical stirrer having a digital controller unit. After each test, the content of gold is determined with atomic absorption.

2. 2. Experimental Design

Taguchi method recommends the use of the loss function to measure the performance characteristics deviating from the desired value [14]. The value of the loss function is further transformed into a signal-to-noise (S/N) ratio. The performance statistics were chosen as the optimization criterion. The performance statistics were evaluated by using the following equation [15]:

$$S/N_l = -10\ log\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{Y_{ijk}^2}\right) \tag{2}$$

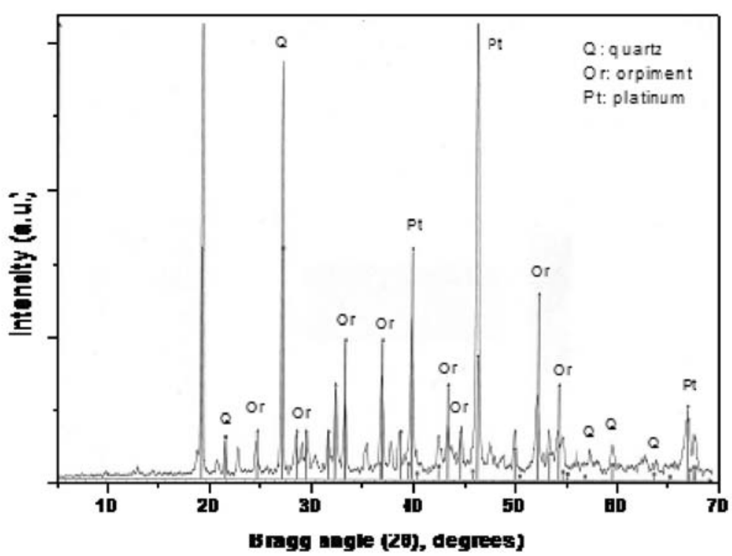

Fig. 1. X-ray diffraction of the ore used in the study.

Table 2. L_9 (3^4) randomize experimental plan table.

Test NO	Parameters and their levels				R 1(%)	R 2(%)	S/N Ratio
	pH	NaCN(ppm)	Solid(%)	Time(h)			
1	10	400	30	20	16.04	15.58	23.98
2	10	800	35	30	24.35	23.74	27.62
3	10	1200	40	40	16.27	17.40	24.51
4	11	400	35	40	10.42	9.77	20.07
5	11	800	40	20	12.97	13.40	22.40
6	11	1200	30	30	21.46	19.62	26.23
7	12	400	40	30	6.92	6.39	16.44
8	12	800	30	40	19.14	20.10	25.85
9	12	1200	35	20	12.12	12.81	21.91

Where S/N_L is the performance characteristic, n the number of repetition performed for an experimental combination and Yi the performance value of ith experiment [14].

We would use S/N_L if the system is optimized when the response is as large as possible, In Taguchi method the experiment corresponding to optimum working conditions might not have been done during the whole period of the experimental stage. In such cases the performance value corresponding to optimum working conditions can be predicted by utilizing the following equation

$$Y_{opt} = \frac{T}{n} + \left(\overline{A_i} - \frac{T}{n}\right) + \left(\overline{B_j} - \frac{T}{n}\right) + \ldots \quad (3)$$

Where n is the total number of trials, T the sum of all responses and $\overline{A_i}, \overline{B_i}$, . . . the average of responses at levels i, j, etc.

The confidence interval at chosen error level may be calculated by:

$$C.I. = \pm\sqrt{\frac{F(1, n_2)V_e}{N_e}} \quad (4)$$

Where F is the value of F table at desired confidence level at degrees of freedom of 1 and degrees of freedom of error, n_2; V_e the variance of error and N_e the effective number of replications. If experimental results are in percentage (%), before evaluating Equations (2) and (3) first omega transformation of percentage values should be applied using the following equation [16 , 17 , 18]:

$$\Omega(dB) = -10\log\left(\frac{1}{P} - 1\right) \quad (5)$$

Where (dB) is the decibel value of percentage value subject to omega transformation and P percentage of the product obtained experimentally [16, 19].

2. 3. Cyanidation Tests

The first series of tests conducted on Zarshuran samples was the diagnostic leaching test. Cyanidation tests were conducted for (24-30 hours) in desired pH (9-11) and solid content of (20-40%) whit (400-600 gr/ton) sodium cyanide. Experimental parameters and their levels were determined using preliminary tests Table 3.

2. 4. Roasting - Cyanidation Tests

The second series of tests, the roast followed by cyanidation leaches, were conducted on Zarshuran samples. The primary purpose of the roast was to oxidize the sulphides present in the ore that may either contain or encapsulate gold or otherwise prevent it from leaching in a standard cyanidation.

The roast procedure also volatilizes the arsenic present in the ore, which dissolves in alkaline solutions to form compounds in solution (e.g. thioarsenites). These compounds reduce Au dissolution by reducing available oxygen in the leach solution, and by forming arsenical films on the surface of the gold.

The arsenic roast was conducted in two, one-hour stages. The first stage was conducted at lower temperature (480 ºC) in a reducing atmosphere to volatilize the arsenic compounds in the ore. The second stage was conducted at higher temperatures (700 ºC) in an oxidizing atmosphere to oxidize the remaining sulphides in the ore.

Once the second stage was completed, the sample was removed from the furnace and allowed to cool. Afterward, the cyanidation tests were conducted on the roasted sample. The cyanidation tests were conducted in the same conditions like first stage tests.

3. RESULTS AND DISCUSSION

The XRD diagram of the sample is presented in figure 1. Also the results of semi-quantitative mineral assemblage of the sample indicated that the main part of sulfide minerals is arsenian sulfide minerals and specially orpiment (As_2S_3) and realgar (AsS) (table 1).

The results of Systematic gold particle identification (gold scan) indicated those visible gold-bearing minerals were not observed in the samples. The lack of visible gold particles and the occurrence of sulfides minerals rich in arsenic and antimony suggests that a large fraction of the gold in the submitted samples occurs as invisible

Table 3. Experimental parameters and their levels.

Factor	S	DOF(f)	V(S/f)	F(V/Ve)	S´	P (%)
pH	24.12	2	12.06	-	24.117	25.178
NaCN(gr/ton)	43.83	2	21.91	-	43.832	45.76
Solid (%)	26.89	2	13.44	-	26.875	28.057
Time(h)	0.96	2	0.48	-	0.96	1.004
Error	0	0	0	-	0	0
Total	95.79	8	-	-	-	100

solid solution gold in sulfide minerals, and particularly in the As rich sulfides phases, including orpiment grains.

3. 1. Cyanidation Tests

The collected data were analyzed by an EXCEL program to evaluate the effect of each parameter on the optimization criteria. Table 4 shows the results and corresponding calculated S/N data for the purification of leach liquor based on $L_9\,(3^4)$ matrix design. To use the S/N ratio for the optimal dissolution performances, S/N calculation was performed to maximize the recovery of gold from the ore.

Analysis of variance (ANOVA) is used to determine the factors that influence on the signal-to-noise ratio. The collected data were analyzed by an EXCEL program. Sum of squares (*S*), mean square (variance), *F* (variance ratio), *S′* (pure sum of squares) and *P* (percentage contribution on response) based on S/N_L for recoveries of gold are presented in Tables 5. According to these results concentration of NaCN has the greatest effect on S/N_L. The *F*-value of all factors except time are greater than the extracted *F*-value from the table for 95% confidence level (The confidence interval for 5% risk is 4.23). This means that the variance of all factors is significant compared with the variance

Table 4. Results and corresponding calculated SNS's.

Factor	S	DOF(f)	V(S/f)	F(V/Ve)	S´	P (%)
pH	24.12	2	12.06	25.065	23.16	24.18
NaCN(gr/ton)	43.83	2	21.91	45.55	42.87	44.76
Solid (%)	26.89	2	13.44	27.931	25.913	27.07
Time(h)	Pooled					
Error	0.96	2	0.48	-	-	4.019
Total	95.79	8	-	-	-	100

Table 5. ANOVA analysis results for all factors.

Factors	Optimum working conditions
pH	10
Sodium Cyanide (gr/ton)	800
Percent Solid (%)	30
Time (Hours)	40
Predicted recovery of gold	29.56%
observed recovery of gold	30.11%, 29.08% and 29.86%.
Predicted confidence interval for recovery of gold	26.35-34.26

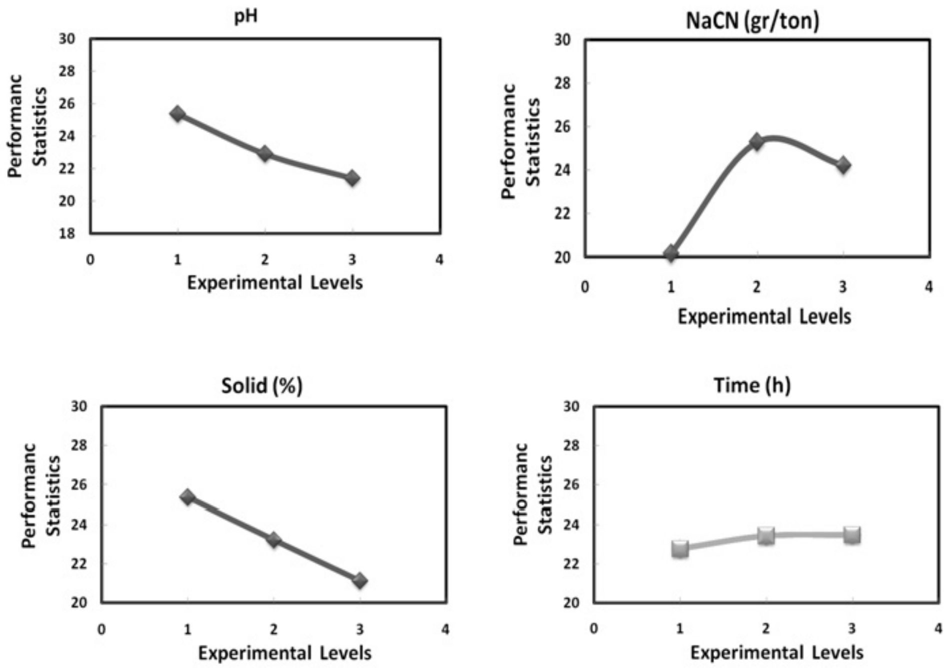

Fig. 2. Main effects plot for S/N ratios of pH, cyanide consumption, and percent solid and time.

of error and all of them have a meaningful effect on the responses. Finally, using these findings and modeling significant effects by the Taguchi method, results for all combination of levels could be predicted. Then these predictions should be confirmed by some experiments. So with spending less time and cost, acceptable results can be derived.

The Taguchi method uses graphs of the marginal means of each factor, as shown in Figure 2. The usual approach is to examine the graphs and pick the winner. The order of graphs in Figure 1 are according to the degree of the influence of parameters on the performance statistics. The performance statistics value of the first data point is thus the average of those obtained from experiments with experiment Number 1–3. Experimental conditions for the second data point therefore are the conditions of the experiments for which column Z is 2 (i.e. experiments with experiment Number 4–6, and so on.

According to these figures, increasing of pH and percent solid decreases the S/NL and But S/NL and mean response first decrease and then increase for the NaCN concentration parameter. Also increasing of time increases the S/N_L.

The numerical value of the maximum point in each graph marks the best value of that particular parameter and is given in Table 6 for each parameter.

In order to test this predicted result, confirmation experiments have been carried out three times at optimum working conditions. The results of these tests were 30.11%, 29.08% and 29.86%.

3. 2. Raost-Cyanidation Tests

Table 7 shows the results and corresponding calculated SNS data for the purification of leach liquor based on L_9 (3^4) matrix design. To use the S/N ratio for the optimal dissolution performances, SNS calculation was performed to maximize the recovery of gold from the ore.

Analysis of variance (ANOVA) is used to determine the factors that influence on the signal-to-noise ratio. The collected data were analyzed by an EXCEL program. Sum of squares (S), mean square (variance), *F* (variance ratio), *S′* (pure sum of squares) and *P* (percentage contribution on response) based on S/N_L for

Table 6. Optimum working conditions, predicted dissolved quantity of gold for direct cyanidation.

Test NO	Parameters and their levels				R 1(%)	R 2(%)	S/N Ratio
	pH	NaCN(ppm)	Solid(%)	Time(h)			
1	10	400	30	20	13.92	21.77	24.40
2	10	800	35	30	15.77	22.51	25.23
3	10	1200	40	40	23.87	24.59	27.68
4	11	400	35	40	22.87	16.24	25.45
5	11	800	40	20	12.81	30.79	24.47
6	11	1200	30	30	28.04	20.55	27.40
7	12	400	40	30	27.01	16.68	26.05
8	12	800	30	40	24.42	18.67	26.43
9	12	1200	35	20	31.05	28.23	29.41

Table 7. Results and corresponding calculated SNS's.

Factor	S	DOF(f)	V(S/f)	F(V/Ve)	S´	P (%)
pH	4.66	2	2.33	-	4.66	21.45
NaCN(gr/ton)	15.97	2	7.99	-	15.97	73.59
Solid (%)	0.78	2	0.39	-	0.78	3.61
Time(h)	0.29	2	0.15	-	0.29	1.35
Error	0.00	0	0.00	-	-	0.00
Total	22	8	-	-	21.70	100.00

recovery of gold is presented in Tables 8. According to these results concentration of NaCN has the greatest effect on S/N_L. The F-value for pH and concentration of NaCN are greater than the extracted F-value from the table for 95% confidence level ($F_{0.05}(1,2) = 4.26$). This means that the variances of pH and concentration of NaCN are significant compared with the variance of error and these factors have a meaningful effect on the responses.

The Taguchi method uses graphs of the marginal means of each factor, as shown in Figs. 2.

According to these figures, for the pH and NaCN parameters, S/N increase with increasing these parameters.

The numerical value of the maximum point in each graph marks the best value of that particular parameter and is given in Table 9 for each

Table 8. ANOVA analysis results for all factors.

Factor	S	DOF(f)	V(S/f)	F(V/Ve)	S′	P (%)
pH	4.650	2	2.33	8.65	4.12	18.97
NaCN(gr/ton)	15.970	2	7.99	29.68	15.44	71.11
Solid (%)	pooling					
Time(h)	pooling					
Error	1.076	4	0.30	-	-	9.92
Total	21.706	8	-	-	-	100.00

Table 9. Optimum working conditions, predicted dissolved quantity of gold.

Factors	Optimum working conditions
pH	12
Sodium Cyanide (gr/ton)	1200
Percent Solid (%)	35
Time (Hours)	40
Predicted recovery of gold	29.179%
observed recovery of gold	31.25%, 29.44% and 30.86%.
Predicted confidence interval for recovery of gold	26.472-31.269

parameter. That is, parameter values given in Table 9 are the optimum conditions.

In order to test this predicted result, confirmation experiments have been carried out three times at optimum working conditions. The results of these tests were 31.25%, 29.44% and 30.86%.

4. CONCLUSIONS

The effect of operating conditions such as pH, sodium cyanide concentration(g/ton), solid content(%) and time(h) on recovery of gold by both cyandiation and roasting- cyanidation was studied with the Taguchi method using an L_9 (3^4) orthogonal array.

The main conclusions can be derived from this study are as follows:

- Relation to the direct cyanidation, it can be stated that:

1. All the parameters have the same effect on the dissolution of gold by cyanidation method.
2. The increasing of pH and percent solid causes the decrease of gold dissolution.
3. The dissolution of gold has a maximum

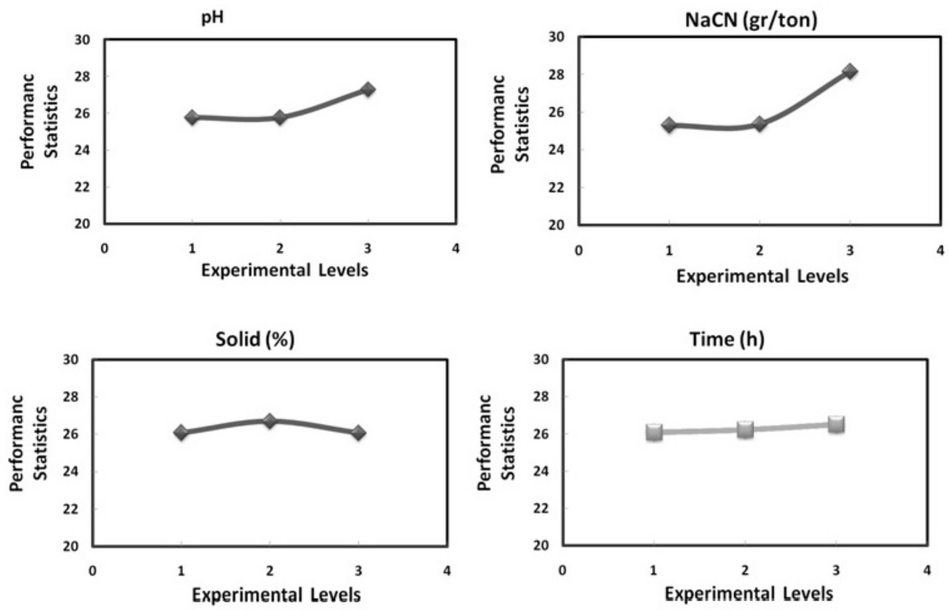

Fig. 3. Main effects plot for S/N ratios of pH, cyanide consumption, and percent solid and time.

after 30 hour but afterward increase very slowly.

4. The maximum dissolution of gold is 30.1% and achieved in the (T=40h), (percent solid=30%), (pH=10) and cyanide content = 800 gr/t).

- Relation to the roasting- cyanidation, it can be stated that :
- Cyanide concentration has the maximum effect on the gold dissolution and pH is the second important factor in this regard.
- The dissolution of gold reached to a maximum at pH about 12 and cyanide content about 1200 grams per ton.
- The amount of gold dissolution reach to a maximum at 35% percent but variation in other percent solid is not very significant.
- The increasing of time causes very slow increase in the gold dissolution.
- The maximum dissolution of gold is 31.25% and achieved in the (T=40h), (percent solid=35%), (pH= 12) and cyanide content = 1200 g/ton).

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